A REVIEW OF MICROBIALLY INDUCED CORROSION (MIC) OF STEEL AND A PRELIMINARY INVESTIGATION TO DETERMINE ITS OCCURRENCE IN NAVAL VESSELS

JOHN F. UPSHER

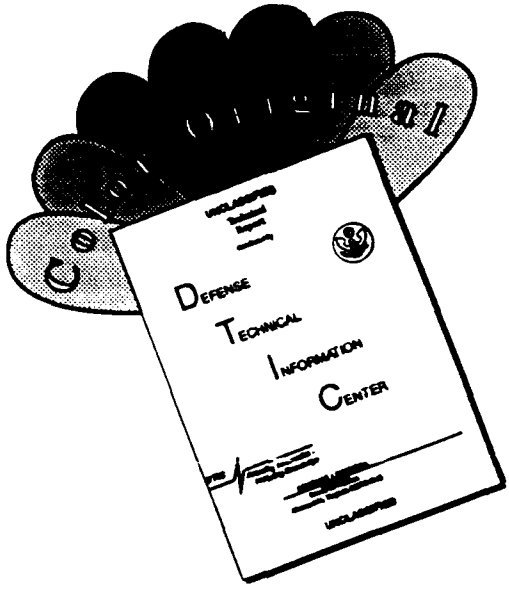
MRL-GD-0048

MAY 1993

MATERIALS RESEARCH LABORATORY

DSTO

DISCLAIMER NOTICE



THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF COLOR PAGES WHICH DO NOT REPRODUCE LEGIBLY ON BLACK AND WHITE MICROFICHE.

A Review of Microbially Induced Corrosion (MIC) of Steel and a Preliminary Investigation to Determine its Occurrence in Naval Vessels

John F. Upsher

MRL General Document
MRL-GD-0048

Abstract

A study was made of the mechanisms of microbially induced corrosion of steels and of influencing factors. The main causative organisms were the sulfate reducing bacteria (SRB) which require little more than a wet situation with depleted oxygen, some small organic molecules and sulfate. The corrosive effect is primarily by cathodic depolarization but local abundance of sulfide and pH change are also involved. SRB were detected at one third of the corrosion sites examined on three Naval ships. They were also present in their oily water wastes which would be a source of infection of any exposed steel surfaces. Based on current information, no special measures to counter microbially induced corrosion of ship steel are recommended but antibacterial treatments warrant further investigation as remedial measures for active microbially induced corrosion (MIC) areas.

DEPARTMENT OF DEFENCE
DSTO MATERIALS RESEARCH LABORATORY

Published by

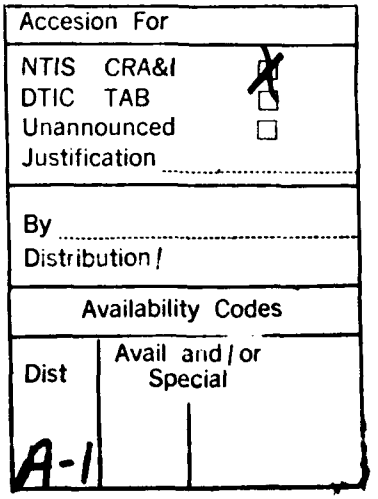
DSTO Materials Research Laboratory
Cordite Avenue, Maribyrnong
Victoria, 3032 Australia

Telephone: (03) 246 8111
Fax: (03) 246 8999

AR No. 008-241

APPROVED FOR PUBLIC RELEASE

Contents



A Review of Microbially Induced Corrosion (MIS) of Steel and a Preliminary Investigation to Determine its Occurrence in Naval Vessels

1. Introduction

Corrosion of the steel of ship hulls is a major cause of costly and lengthy drydocking during refit (Berning, McGovern and Goodwin, 1981; Bleile and Rodgers, 1984). Whereas the process of corrosion, i.e. the dissolution of metal, principally iron, is traditionally considered in electrochemical terms, the past decade has shown an increasing awareness that micro-organisms have an active role in initiating and accelerating the process. The present study was undertaken in order to review published information on microbially induced corrosion (MIC) and to relate it to corrosion on Australian naval ships.

The electrochemical processes involved in the complex phenomenon of MIC have been extensively investigated (Dowling, Guezennec and White, 1988; Duquette and Ricker, 1985; Iverson, Olsen and Heverly, 1985; Little, Wagner and Gerckachov, 1985; Pederson and Hermansson, 1989; Pope, 1985; Robinson, Parker and Seal, 1987; Tiller and Corr, 1985; Tomei and Mitchell, 1985; Videla, 1985) and reviewed (Hamilton, 1985; Hamilton and Maxwell, 1985; Iverson, 1987; Miller, 1981; Pope, 1983; Rogers, 1948; Tiller, 1983; Videla, 1988, 1991) so that the role of microorganisms in inducing, accelerating and sustaining the corrosion process is now well established.

Seawater is known to be corrosive to many steels (Davies and Case, 1986) but with additional microbial influence the process can be so severe as to cause serious problems in the offshore oil industry (Battersby, Stewart and Sharma, 1985; Kasahara and Kajiyama, 1985; Maxwell and Hamilton, 1985; Walch and Mitchell, 1984; Weimer, van Kavelaar, Michel and Ng, 1988), other marine installations (Campbell, Scannell and Walsh, 1990; Dexter, Lucas and Gao, 1985; Edyvean, 1991; Eidsa and Risberg, 1985), and in ships (Campbell *et al.* 1990; Melton and Bodnar, 1988).

Corrosion of the exterior of steel hulls of ships is an inevitable consequence of a breach of the protective coating and is often associated with the presence of surface growths of fouling organisms (Edyvean, Thomas and Brook, 1988; Sanders and Maxwell, 1983; Videla and Characklis, 1982). Possibly of greater significance is the more localised and more invasive corrosion that occurs on the inner surfaces of the hull and ship structure. It is almost axiomatic that ships rust from the inside, hence the relentless program of repainting of internal steel surfaces.

Conventional measures employed to prevent and control corrosion of steel, are based wholly on the understanding of the electrochemical process. They include the use of chemical treatments which place a passive film on the metal surface, together with the application of surface coatings to place a barrier between the metal and the environment. Such methods are effective only so long as there are no breaks in the surface protection. The more recent measure of fitting sacrificial anodes of aluminium or zinc to hull exteriors does not confer protection against MIC of inner surfaces in contact with internal water bodies such as bilges, oily water wastes or condensate (Maxwell and Hamilton, 1985; Parker, Seal and Robinson, 1988; Robinson *et al.* 1987).

In view of the continuing incidence of steel corrosion in Naval ships, this investigation was undertaken to ascertain the role and significance of microorganisms so that, if they were found to play a major role, alternative preventive measures might then be considered. It was first necessary to evaluate the published material on aspects of MIC affecting steels then to examine corrosion samples from different sites on Naval ships for evidence of bacterial implication in the corrosion process.

2. *The Corrosion Process in Ferrous Metals and Mechanisms of Bacterial Interaction*

Corrosion is the electrochemical reaction in which a metal dissolves in its aqueous environment. Electrons and metal ions are formed at an anodal site: the electrons flow to another metal (cathode) or to some other electron sink. The process thus constitutes an electrochemical cell, as shown here for ferrous metals.

Iron dissolution:	$4Fe \rightarrow 4Fe^{2+} + 8e^{-}$ (Anode)
Water dissociation:	$3H_2O \rightarrow 8H^{+} + 8OH^{-}$
Hydrogen reduction:	$8H^{+} + 8e^{-} \rightarrow 8H$ (Cathode)

Microbial corrosion follows the same electrochemical mechanisms as the non-biological process but the microbial role is to stimulate or to affect an anodic or cathodic reaction or to assist in the establishment of an electrolytic cell.

Bacteria were first implicated in the corrosion of ferrous metals in anoxic conditions by von Wolzogen Kuhr and van der Vlugt (1934) who recognised the role of the anaerobic sulfate reducing bacteria (SRB). They also proposed the probable mechanism for the attack based on the ability of these bacteria to oxidise the protective film of hydrogen on the metal surface. This process was called cathodic depolarisation and has been regarded as central to the mode of SRB action (Chatelus, Carrier, Saignes, Libert, Berlier, Lespinat, Fauque and LeGall,

1987; Little, Wagner and Duquette, 1988; Parker *et al.* 1988; Peck, LeGall, DerVartanian, Moura, Moura, Xavier and Huyh, 1983; Robinson *et al.* 1987). The process is represented as follows:

Microbial consumption of hydrogen (cathodic depolarisation):

$$SO4^{2-} + 8H \rightarrow S^{2-} + 4H_2O$$

Corrosion products:

$$Fe^{2+} + S^{2-} \rightarrow FeS$$
$$3Fe^{2+} + 6OH^{-} \rightarrow 3Fe(OH)_2$$

More recently, some additional theories and mechanisms have been proposed to occur during anaerobic corrosion of iron and steels and corrosion mechanisms that result in products containing iron phosphate, vivianite, ($Fe_2(PO_4)_2.8H_2O$), crystalline mackinawite, (Fe_2S_8), and goethite (FeO(OH)) have been proposed (Weimer *et al.* 1988). A number of complex reactions that are likely to occur as a consequence of the heterogeneity of the biofilm have also been indicated (Ford, Maki and Mitchell, 1988). Thus, several mechanisms that may be activated by the conditions prevailing at the metal surface supplement the dominant cathodic polarisation mechanism and modify the composition of the corrosion product (Ford *et al.* 1988; Iverson and Olson, 1983; Iverson *et al.* 1985; Weimer *et al.* 1988).

Some genera of aerobic bacteria have also been implicated in corrosion of ferrous metals, including *Vibrio, Serratia* and *Pseudomonas* (Gaylarde and Videla, 1987; Little *et al.* 1988; Pederson and Hermansson, 1989; Pope, 1985; Westlake, Semple and Obuekwe, 1985) and presumably other aerobic and fermentative genera. The corrosive action of the aerobes is largely through acidic metabolic products and creation of corrosion cells. In constantly aerobic situations where there are oxidisable sulfur sources, the sulfur-oxidising thiobacilli, e.g. *Thiobacillus*, produce sulfuric acid. Several oxidising reactions involving most inorganic sulfur compounds have been identified (Cragnolino and Tuovinan, 1984; Kuonan and Tuovinen, 1981; Roy and Trudinger, 1970). Whereas the processes of MIC have been observed and rationalised in a wide variety of situations and with several types of microorganisms, either singly or in combination, the most aggressive mode of attack is by the SRB in conditions which are locally anaerobic. This form of corrosion usually results in deep pitting and the formation of black, iron sulfide as a primary corrosion product. In naval ships, where the contact water generally contains sulfate from seawater and serious deep pitting corrosion occurs, then SRB-related corrosion was thought to be the major cause.

Videla (1988) summarised the features of MIC, stating "the complexity of biological environments involved with SRB activity make it very difficult to assess a microbial effect by means of electrochemical methods when the chemical composition and pH of the medium is continuously varying due to microbial metabolism", and that "under these circumstances the explanation must include the breakdown of passivity by metabolic products of aggressive characteristics poured into the medium by microbial activity."

The corrosion-inducing bacteria are invariably on the metal surface in an heterogeneous layer, the biofilm. The biofilm consists essentially of an organic fibrous-gelatinous matrix secreted by microbial cells; several different species may be present together. The characteristics of the biofilm in relation to its role in corrosion have been reviewed (Beech and Gaylarde, 1991; Boivin and

Costerton, 1991; Characklis, 1989; Cragnolino and Tuovinen, 1984; Crombie, Moody and Thomas, 1980; Ford *et al.* 1988; Gaylarde and Beech, 1991; Geesey, Mittelman, Iwaoka and Griffiths, 1986; Gilbert, Attwood, Morgan and Herbert, 1987; Hamilton, 1985; Lee and Characklis, 1991; Videla, 1991). The main factors by which the biofilm is instrumental in corrosion of steel are that:

(a) growth of bacteria is enhanced by the tendency of the gel matrix to absorb and retain nutrients from the adjacent water;

(b) growth of SRB in particular is enhanced by the retention of metabolites produced by the aerobic bacteria, which are then available as nutrients for the SRB;

(c) aerobic bacteria present in the biofilm utilise available oxygen so that inner layers of the biofilm remain anaerobic, and

(d) corrosion is enhanced by the local and localised retention of sulfide and lowered pH.

3. *Factors Influencing the Activity of Bacteria Implicated in Steel Corrosion*

3.1 *General*

Although a number of aerobic and fermentative water-borne bacteria, are able to facilitate some degree of corrosion of ferrous metals, it is the SRB which are implicated in almost all major incidents in water and soil and particularly where anaerobiosis is sustained at the metal surface (Crombie *et al.* 1980; Hamilton, 1983, 1985; Hardy and Brown, 1987; King and Miller, 1971; Starkey, 1985). This report will thus review the biology and physiology of the SRB and the conditions impinging on SRB activity which prevail in corrosion-susceptible areas of ships.

3.2 *Temperature*

The temperatures of ship hulls and attached structures are largely dependent upon the temperature of the surrounding sea. Although sea temperatures from 0 to 35°C are possible, sea surface temperatures in Australian waters generally range between 12 and 30°C (J. Lewis, DSTO-MRL, personal communication). Temperatures of internal structures are more influenced by nearby installations such as machinery and to a lesser extent by the atmosphere, therefore with the exception of areas of local heating, the internal temperature would not be expected to exceed about 35°C.

The majority of SRB species have moderate temperature requirements for growth, usually between 10 and 45°C (Postgate, 1984; Widdel, 1988), though there are some thermophilic species capable of growth above 55°C (Widdel, 1988) and of causing corrosion at elevated temperatures (Ford, Walch and Mitchell,

1987). SRB isolates from Naval bilges and oily water wastes had temperature optima between 35 and 40°C with maxima between 40 and 45°C (Upsher, Hodgeman and Fletcher, 1993). Thus the temperature of shipboard steel structures would generally be conducive to SRB activity. Growth would be reduced at lower temperatures, i.e. below 15°C, and suspended below about 10°C.

3.3 *pH Effects*

The pH range for growth of SRB isolates from bilges and oily water wastes was 6.0 to 8.0 (Upsher *et al.* 1993) and the pH of more than 90% of those fluids examined was also within that range (Hodgeman, Upsher and Fletcher, 1993). It is anticipated that unless the pH of an oily water waste was made to exceed that range by the introduction of a strongly acidic or alkaline additive such as corrosion treatment solution, the pH of fluids in contact with structural steel components would be close to neutrality and thus conducive to SRB activity.

3.4 *Oxidation-Reduction Potential (ORP)*

SRB are a group of bacteria that can live and grow only in the absence of oxygen and in a reducing environment with an ORP of <-100 mV (Postgate, 1984; Widdell, 1988). In oily water wastes, such anoxic and reducing environments are not unusual. The aerobic bacteria, through their metabolic activity, deplete the oxygen level and the iron/steel surface is itself reducing. Once the anaerobic state is established, the SRB sustain the reducing environment by producing sulfide as a consequence of respiratory reduction of sulfate. Anaerobiosis is constantly being countered by the supply of oxygen from the atmosphere. Only when bacterial activity becomes diminished is the reduced state lost and the environment no longer favourable to the SRB. Within the environment of the OWW, restricted situations such as crevices, and fissures, sludges and sediments remain anaerobic as does the inner layer of the biofilm.

3.5 *Inorganic Nutrients*

In order to sustain growth, the SRB, like most other free-living bacteria, require the presence of a number of elements. These include potassium, magnesium, calcium, sulfur (as sulfate), phosphorus (as phosphate), nitrogen (as ammonium ions or amino acids), together with those elements required in smaller quantities (<~1 ppm), the trace elements iron, copper, manganese, boron, zinc, molybdenum and others. In many aqueous environments these are generally sufficient but they are easily depleted. In sea water, the concentration of phosphorus (phosphate) is so low, at between 0.001 and 0.1 ppm (Sverdrup, Johnson and Fleming, 1942) that it is the first element to restrict microbial growth. Once the vital mineral elements are taken up by the biomass, they are retained there, to be released for recycling on the death of the microorganism. The bacterial cells and the biofilm actively accumulate and retain mineral ions so that the microbiota can continue to thrive, even when the inorganic nutrients are deficient in the ambient medium. Thus in most shipboard situations where water persists, sufficient

mineral nutrients will be available to support a microbial population and to sustain MIC.

3.6 Organic Nutrients

SRB require a limited range of generally simple organic compounds such as lactate, ethanol, pyruvate, propionate, and acetate, to fulfil their energy needs (Postgate, 1984; Widdel, 1988). These are commonly encountered in aqueous environments, where they occur as metabolic products from other bacteria. In this way, SRB are dependent upon other organisms to break down the more complex organic molecules that would not otherwise be available to them.

A molecule can expand its available electrons only once in microbial catabolism, so organic molecules exert a finite influence on SRB activity and a continuous source of fresh organic nutrient is required for sustained activity.

3.7 Salinity

SRB show a range of responses to sodium chloride in their environment; some species are capable of growth in hypersaline conditions (> 5%); some others have a definite requirement for it (1 to 5%) in order to grow (Postgate, 1984; Widdel, 1988). SRB strains isolated from bilge fluids and OWW also showed a range of responses from no requirement to growth at > 5% (Upsher *et al.* 1992). Thus it is not likely that either excess or deficiency of salt would be a critical factor in SRB activity in shipboard corrosion sites except where sea water is allowed to evaporate.

4. Examination of Corrosion Sites on RAN Ships

Three ships were inspected for internal corrosion sites and samples were taken for bacteriological assessment. Two ships were at Garden Island Dockyard, NSW. HMAS Hobart had been in dock for almost three years undergoing a major refit and HMAS Parramatta, had been in dock for several months pending a decision on its future. HMAS Brisbane was inspected during a brief visit to Melbourne. Some of the sites sampled are shown in Plates 1 to 3 in Appendix B. Sites selected and descriptions of the samples taken are detailed in Table 1.

Table 1: *Sample locations and details*

Sample No.	Ship	Sample Site	Sample Description
H1	HMAS Hobart	Engine Room 2: under paint on hull (Plate 1)	Hard black and red corrosion product
H2	HMAS Hobart	Engine Room 2: under paint from flange on hull (Plate 2)	Hard black and red corrosion product
H4	HMAS Hobart	Ablution area, above weld with s/steel floor	Hard black and red corrosion product
H6	HMAS Hobart	Bilge in Engine Room 1	Sediment with corrosion material
H6S	HMAS Hobart	Bilge in Engine Room 1	Swab sample from painted bilge wall, below water level, close to H6
H7	HMAS Hobart	Engine Room 1, under leaking gland of saltwater pump	Black and orange corrosion product
H8	HMAS Hobart	Engine Room 1, tray under seawater pump (Plate 3)	Loose black and orange corrosion product
P1	HMAS Parramatta	Engine Room, on hull under seawater pump	Black corrosion product
P2	HMAS Parramatta	Engine Room, tray under seawater pump	Red and black corrosion products
P3	HMAS Parramatta	Engine Room, on hull	Red and black corrosion products, under paint
P4	HMAS Parramatta	Shower recess	Rust blister formed under recent repaint
P5	HMAS Parramatta	Bilge in Engine Room	Sludge containing corrosion products
P5S	HMAS Parramatta	Painted wall of bilge in Engine Room	Swab sample
P6	HMAS Parramatta	Bilge in Engine Room	Oily water waste
B1	HMAS Brisbane	Engine Room 2: under fuel oil strainer	Black fuel-soaked corrosion products
B2	HMAS Brisbane	Engine Room 2: under fuel oil strainer	Duplicate of B1
B3	HMAS Brisbane	Cold water pipe, passing through bulkhead, had been painted over	Black and red corrosion product
B4	HMAS Brisbane	Bulkhead in Engine Room 2: had been painted over	Black and red corrosion product
B5	HMAS Brisbane	Engine Room: pedestal under water pump	Orange corrosion product
B6	HMAS Brisbane	Engine Room: sloping section of hull under water pump	Loose orange corrosion product
B7	HMAS Brisbane	Engine Room 1	Oily water waste
B8	HMAS Brisbane	Engine Room 2	Oily water waste

5. Methods

5.1 Sampling Methods

Solid samples were taken using sterile instruments and placed into serile screw-cap glass bottles. Swab samples from surfaces below water level were taken using sterile alginate (surgical) swabs, scouring an area of approximately one square centimetre. Swab heads were broken into sterile screw cap glass bottles. Water samples were taken at some distance from the surface but away from any sediment, using sterile 10 ml pipettes. Samples were refrigerated in the laboratory until processing.

5.2 Preparation of Samples

5.2.1 Hard Samples

Approximately 0.1 g of sample was aseptically placed in a sterile biological macerator with 0.5 ml sterile diluent (Maximum Recovery Diluting Fluid, Appendix A) and ground until reduced to a slurry. This was then transferred to 9.5 ml sterile diluent and used in serial decimal dilution; i.e. 1.0 ml, aseptically transferred to 9.0 ml diluting fluid and shaken and the procedure repeated.

5.2.2 Swab Samples

Sterile diluent, 9.0 ml, was introduced to the bottles containing the swab-heads and shaken vigorously. The liquid was then used in serial decimal dilution.

5.2.3 Liquid Samples

Samples were shaken vigorously then allowed to settle for five minutes. 1.0 ml of the suspension was aseptically taken by pipette, not from near the sediment, then added to 9.0 ml of diluent and used in serial decimal dilution.

5.3 Bacteriological Assessment

Aliquots of 1.0 ml from selected dilutions were transferred to petri dishes for assessment of the total count of aerobic bacteria using Nutrient Agar (Oxoid). Tubes of Purple McConkey Broth (Oxoid) were used for determining (presumptive) coliforms and tubes of MRL-SRB Medium for SRB assessment (Appendix A).

All plates and tubes were incubated at 30°C; the coliform tubes were examined after 48 hours; the total count plates after four days and the SRB tubes after two weeks or more.

6. Results and Discussion

Observations of corrosion on board the three ships inspected were restricted for different reasons. On HMAS Hobart, there had been a major overhaul, during which all but the least severe cases had been cut out and replaced. Verbal accounts provided some insight into the extent and appearance of the affected areas that had been removed. Corrosion problems on HMAS Parramatta were relatively slight and there were few sites to be sampled. HMAS Brisbane, on its return to Australian waters, had undergone an extensive re-paint program and although most corrosion areas had been superficially dressed and painted, there were indications that the underlying corrosion remained active and would split and rupture the coating.

Results of the bacteriological assessments are presented in Table 2. Numbers reported indicate the calculated number of viable bacteria (i.e. colony-forming units) present per gram of solid material, per square centimetre for swab samples and per millilitre of liquid samples.

Table 2: *Bacterial content of samples. The figures presented for Total Aerobes are derived from the numbers of colonies observed on the dilution plates. Estimates of SRB and Coliforms are calculated from the observations of dilution tubes.*

Sample		Total Aerobes	SRB	Coliforms
H1	Corrosion product	8.0×10^2	ND	ND
H2	Corrosion product	6.0×10^2	$> 10^2$	ND
H4	Corrosion product	1.6×10^4	ND	ND
H6	Bilge sediment	1.8×10^5	$> 10^3$	$> 10^3$
H6S	Swab sample	2.6×10^5	$> 10^2$	$> 10^3$
H7	Corrosion product	1.2×10^3	ND	ND
H8	Corrosion product	2.3×10^3	ND	ND
P1	Corrosion product	0.7×10^6	$> 10^2$	ND
P2	Corrosion product	1.0×10^5	$> 10^2$	ND
P3	Corrosion product	9.0×10^2	ND	ND
P4	Corrosion product	5.0×10^5	ND	$> 10^2$
P5	Bilge sediment	2.4×10^6	$> 10^2$	ND
P5S	Swab sample	1.4×10^7	$> 10^2$	> 10
P6	OWW	7.9×10^6	ND	ND
B1	Corrosion product	4.4×10^7	$> 10^2$	$> 10^3$
B2	Corrosion product	8.4×10^6	$> 10^2$	$> 10^3$
B3	Corrosion product	4.8×10^3	ND	NA
B4	Corrosion product	0.5×10^3	ND	NA
B5	Corrosion product	$< 10^2$	ND	NA
B6	Corrosion product	6.9×10^4	ND	NA
B7	OWW	9.0×10^6	$> 10^3$	$> 10^3$
B8	OWW	8.3×10^6	$> 10^3$	$> 10^3$

NA = not assessed; ND = not detected.

SRB were isolated from five of the thirteen corrosion product samples which showed some black (sulfide) component. That two of the ships, HMAS Hobart and HMAS Parramatta had been out of service for some time prior to sampling, would have meant that surfaces had less wetting and less contamination through agitation of the bilge fluid and the nett result would have been to reduce or suspend SRB growth. Thus the SRB that were observed and recorded would have been the survivors of a more extensive population.

SRB are recognised as being fastidious and difficult to recover and grow in the laboratory (Postgate, 1984) and numbers observed may often be one or two orders of magnitude less than the number actually present (Stevenson, 1978). Also, with the prolonged restriction of growth on HMAS Hobart and Parramatta, it is reasoned that the SRB results presented here are not only underestimates, but indicate a much larger presence at some earlier time. Consequently, a "not detected" result does not mean that none were present and it is thus probable that samples H1, H4, H7, P3, P4, B3 and B4, which all contained some iron sulfide, would at some earlier time have had active SRB populations.

SRB were present in significant numbers in the oily-water wastes, bilge sediments, biofilm (swab) samples and submerged aggregates of corrosion products, indicating large and persistent sources of corrosion-causing bacteria present in each ship.

7. Conclusions and Recommendation

The published literature provides overwhelming evidence that the activities of bacteria are instrumental in initiating or accelerating the corrosion process, which is referred to as "microbially induced corrosion" (MIC). It is of widespread occurrence, but is particularly severe where anoxic conditions persist on a ferrous metal surface and in the presence of available sulfate and traces of certain dissolved organic compounds. Given these conditions, SRB prevail and have the potential to cause deep pitting corrosion. Corrosion products formed by SRB-activity are often blackened by iron sulfides. MIC is a severe problem in marine installations, where sulfate is present in seawater and has the potential to affect the economics of the offshore oil industry, causing structural failure.

Three naval ships were examined for corrosion and samples were taken from representative sites. Because two of the ships had not been in active service prior to examination and because of the physiology of the SRB, estimates of bacterial activity were recognised as being less than would normally be present. Nevertheless, more than one third of samples of corrosion products with some blackening showed the presence of live SRB. This indicated a widespread occurrence of these corrosion-inducing bacteria with the potential to cause severe pitting. On HMAS Hobart, all large corrosion areas had been cut out and replaced so examples of the most severe corrosion could not be examined or assessed.

From consideration of published material, together with anecdotal evidence collected at the times of examining the ships, and the limited microbiological evidence presented here, it is highly probable that MIC is involved in most internal hull and structural steel corrosion and could account for the most severe examples. SRB and other bacteria were also abundant in bilge fluids, sludge and

corrosion aggregates, which would constitute a constant source of infection of exposed metal with the potential to initiate new corrosion centres.

Given the presence of SRB and their activity in initiating or accelerating corrosion of steel in naval ships, some consideration should be given to determine the most appropriate measures for prevention and control and their cost-effectiveness. Treatments aimed at killing corrosion bacteria or inhibiting their growth could be examined for long-term effectiveness with a view to establishing a procedure for permanent inactivation of deep MIC sites.

8. Acknowledgements

I wish to record my gratitude to Lt B. Ogrizek of HMAS Hobart and to the crew members of HMAS Hobart, HMAS Parramatta and HMAS Brisbane who assisted on the inspection visits. Thanks are also extended to Mr B. Smith (DSTO-MRL) for valuable discussion and camera work.

9. References

Battersby, N.S., Stewart, J.D. and Sharma, A.P. (1985).
Microbial problems in the offshore gas and oil industries. *Journal of Applied Bacteriology*, Symposium supplement, pp. 2279-2356.

Beech, I.B. and Gaylarde, C.C. (1991).
Microbial polysaccharides and corrosion. *International Biodeterioration*, 27, pp. 95-108.

Berning, J.A., MacGovern, R.N. and Goodwyn, S.C. (1981).
Ship overhaul effectiveness. (Report No. CNS-1157). Alexandria, VA: Center for Naval Analyses, Institute of Naval Studies.

Bleile, H.R. and Rodgers, S.D. (1984).
Shipboard corrosion engineering. 21st Annual Technical Symposium, Association of Scientists and Engineers of the Naval Sea Systems Command, Washington, DC.

Biovin, J. and Costerton, J.W. (1991).
Biofilms and biodeterioration. In *Biodeterioration and Biodegradation*, 8, ed. H.W. Rossmoore, pp. 53-61. London: Elsevier.

Campbell, S.A., Scannell, R.A. and Walsh, F.C. (1990).
Microbially assisted pitting of ship's hull plate. *Industrial Corrosion*, 8, pp. 1-14.

Characklis, W.G. (1989).
Biofilm and corrosion: a process analysis viewpoint. *International Biodeterioration*, **25**, pp. 323-326.

Chatelus, C., Carrier, P., Saignes, P., Libert, M.F., Berlier, Y., Lespinat, P.A., Fauque, G. and LeGall, J. (1987).
Hydrogenase activity in aged non-viable *Desulfovibrio vulgaris* cultures and its significance in anaerobic biocorrosion. *Applied and Environmental Microbiology*, **53**, pp. 1708-1710.

Cragnolino, G. and Tuovinen, D.H. (1984).
The role of sulphate-reducing and sulphur-oxidizing bacteria in the localized corrosion of iron-based alloys - a review. *International Biodeterioration*, **20**, pp. 9-26.

Crombie, D.J., Moody, G.J. and Thomas, J.D.R. (1980). Corrosion of iron by sulphate-reducing bacteria. *Chemistry and Industry*, June 1980, pp. 500-504.

Davies, J.D. and Case, B. (1986).
Microbiological effects on galvanic corrosion in seawater. *UK Corrosion* , **86**, pp. 35-42.

Dexter, S.C., Lucas, K.E. and Gao, G.Y. (1985).
The role of marine bacteria in crevice corrosion initiation. In *Biologically Induced Corrosion*, ed. S.C. Dexter, pp. 144-151. Houston, Texas: NACE.

Dowling, N.J.E., Guezennec, J. and White, D.C. (1988).
Methods for insight into mechanisms of microbially influenced metal corrosion. In *Biodeterioration*, **7**, eds. D.R. Houghton, R.N. Smith and H.O.W. Eggins, pp. 404-410. London: Elsevier.

Duquette, D.J. and Ricker, R.E. (1985).
Electrochemical aspects of microbiologically induced corrosion. In *Biologically Induced Corrosion*, ed. S.C. Dexter, pp. 121-130. Houston, Texas: NACE.

Edyvean, R.G.J. (1991).
Fouling and corrosion – the offshore experience. In *Biodeterioration and Biodegradation*, **8**, ed. H.W. Rossmoore, pp. 588-590. London: Elsevier.

Edyvean, R.G.J., Thomas, C.J. and Brook, R. (1988).
The effect of marine fouling on corrosion-fatigue of offshore structures. In *Biodeterioration*, **7**, eds. D.R. Houghton, R.N. Smith and H.O.W. Eggins, pp. 385-390. London: Elsevier.

Eidsa, G. and Risberg, E. (1985).
Sampling for the investigation of sulfate reducing bacteria and corrosion on offshore structures. In *Biologically Induced Corrosion*, ed. S.C. Dexter, pp. 109-120. Houston, Texas: NACE.

Ford, T.E., Maki, J.S. and Mitchell, R. (1988).
Involvement of bacterial exopolymers in biodeterioration of metals. In *Biodeterioration*, **7**, eds. D.R. Houghton, R.N. Smith and H.O.W. Eggins, pp. 378-384. London: Elsevier.

Ford, T.E., Walsh, M. and Mitchell, P. (1987).
Corrosion of metals by thermophilic microorganisms. *Materials Performance*, **26**(2), pp. 35-39.

Gaylarde, C.C. and Beech, I.B. (1991). Relevance of biofilms and EPS to metal corrosion. In *Biodeterioration and Biodegradation*, **8**, pp. 585-586. London: Elsevier.

Gaylarde, C.C. and Videla, H.A. (1987).
Localised corrosion induced by a marine *Vibrio*. *International Biodeterioration*, **23**, pp. 91-104.

Geesey, G.G., Mittelman, M.W., Iwaoka, T. and Griffiths, P.R. (1986). Role of bacterial exopolymers in the deterioration of copper surfaces. *Materials Performance*, **25**(2), pp. 37-40.

Gilbert, P.D., Attwood, P.A., Morgan, T.D.B. and Herbert, B.N. (1987). Biofilm associated corrosion. *UK Corrosion*, **87**, pp. 291-308.

Hamilton, W.A. (1983). The sulphate reducing bacteria: their physiology and consequent ecology. *Microbial Corrosion*, **83**, pp. 1-5.

Hamilton, W.A. (1985). Sulphate reducing bacteria and anaerobic corrosion. *Annual Review of Microbiology*, **39**, pp. 195-217.

Hamilton, W.A. and Maxwell, S. (1985). Biological and corrosion activities of sulphate-reducing bacteria within natural biofilms. In *Biologically Induced Corrosion*, ed. S.C. Dexter, pp. 131-136. Houston, Texas: NACE.

Hardy, J.A. and Brown, J.L. (1987). Sulphate-reducing bacteria – their contribution to the corrosion process. *Industrial Corrosion*, March 1987, pp. 8-10.

Hodgeman, D.K.C., Upsher, F.J. and Fletcher, L.E. (1993).
Hydrogen sulfide generation in shipboard oily water wastes: Part 4: Ship factors (MRL Technical Report MRL-TR-93-20). Maribyrnong, Vic.: Materials Research Laboratory.

Iverson, W.P. (1987).
Microbial corrosion of metals. Advances in *Applied Microbiology*, **32**, pp. 1-36.

Iverson, W.P. and Olson, G.J. (1983).
Anaerobic corrosion by sulfate-reducing bacteria due to a highly reactive volatile phosphorus compound. *Microbial Corrosion*, **83**, pp. 46-53.

Iverson, W.P., Olson, G.J. and Haverly, L.F. (1985). The role of phosphorus and hydrogen sulfide in the anaerobic corrosion of iron and the possible detection of this corrosion by an electrochemical noise technique. In *Biologically Induced Corrosion*, ed. S.C. Dexter, pp. 154-161. Houston, Texas: NACE.

Kasahara, K and Kajiyama, F. (1985).
Role of sulfate reducing bacteria in the localized corrosion of buried pipes. In *Biologically Induced Corrosion*, ed. S.C. Dexter, pp. 171-177. Houston, Texas: NACE.

King, R.A. and Miller, J.D.A. (1971).
Corrosion by the sulphate-reducing bacteria. *Nature*, **223**, pp. 491-492.

Kuonen, J.G. and Tuovinen, D.H. (1981). The genera *Thiobacillus* and *Thiomicrospira*. In *The Prokaryotes, a Handbook of Habitats, Isolation and Identification of Bacteria*, eds. M.P. Starr *et al.*, pp. 1023-1026. New York: Springer.

Lee, W.C. and Characklis, W.G. (1991).
Anaerobic corrosion processes of mild steel in the presence and absence of anaerobic biofilm. In *Biodeterioration and Biodegradation*, **8**, pp. 89-111. ed. H.W Rossmoore. London: Elsevier.

Little, B., Wagner, P. and Duquette, D. (1988).
Microbiologically induced increase in corrosion current density of stainless steel under cathodic protection. *Corrosion-NACE*, **44**, pp. 270-274.

Little, B., Wagner, P. and Gerckachov, S.M. (1985).
A quantitative investigation of mechanisms for microbial corrosion. In *Biologically Induced Corrosion*, pp. 209-216. Ed. S.C. Dexter. Houston, Texas: NACE.

Maxwell, S. and Hamilton, W.A. (1985).
The activity of sulphate-reducing bacteria on metal surfaces in an oilfield situation. In *Biologically Induced Corrosion*, **85**, pp. 284-290. Ed. S.C. Dexter. Houston, Texas: NACE.

Melton, T. and Bodnar, J.W. (1988).
Marine biology of marine microorganisms: biotechnological approaches to naval problems. *Naval Research Reviews*, **XL**, pp. 1-39.

Miller, J.D.A. (1981).
Corrosion by the sulphate reducing bacteria. In *Microbial Deterioration*, pp. 179-202. Ed. A.H. Rose. London: Academic Press.

Parker, C.H.J., Seal, K.J. and Robinson, M.J. (1988).
Hydrogen absorption during the microbial corrosion of steel. In *Biodeterioration*, **7**, pp. 391-397. Eds. D.R. Houghton, R.N. Smith and H.O.W. Eggins. London: Elsevier.

Peck, H.D., LeGall, J., DerVartanian, D.V., Moura, I., Moura, J.J., Xavier, A.V. and Huyh, B.H. (1983).
Hydrogenase and hydrogen metabolism in the sulfate-reducing bacteria *Desulfovibrio*. *Microbial Corrosion*, pp. 6-15.

Pederson, A. and Hermansson, M. (1989).
The effects on metal corrosion by *Serratia marcescens* and a *Pseudomonas* sp. *Biofouling*, **1**, pp. 313-322.

Pope, D.H. (1985).
Discussion of methods for the detection of microorganisms involved in microbiologically influenced corrosion. In *Biologically Induced Corrosion*, ed. S.C. Dexter, pp. 275-282. Houston, Texas: NACE.

Postgate, J.R. (1984).
The Sulphate-Reducing Bacteria. 2nd ed. Cambridge: Cambridge University Press.

Robinson, M.J., Parker, C.H.J. and Seal, K.J. (1987).
The influence of sulphate reducing bacteria on hydrogen absorption by cathodically protected steel. *UK Corrosion*, **87**, pp. 279-289.

Rogers, T.H. (1948).
The promotion and acceleration of metallic corrosion by microorganisms. *Journal of Industrial Metals*, **75**, pp. 19-38.

Roy, A.B. and Trudinger, P.A. (1970).
The Biochemistry of Inorganic Compounds of Sulphur. Cambridge: Cambridge University Press.

Sanders, P.F. and Maxwell, S. (1983).
Microfouling, macrofouling and corrosion of metal test specimens in seawater. *Microbial Corrosion*, **1983**, pp. 74-83. Teddington.

Starkey, R.L. (1985).
Anaerobic corrosion – perspectives about causes. In *Biologically Induced Corrosion*, pp. 3-7. Ed. S.C. Dexter. Houston, Texas: NACE.

Stevenson, L.N. (1978).
A case for bacterial dormancy in aquatic systems. *Microbial Ecology*, **4**, pp. 127-133.

Sverdrup, H.U., Johnson, M.W. and Fleming, R.H. (1942).
The oceans: Their physics, chemistry and general biology, pp. 239-241. Englewood Cliffs, N.J.: Prentice-Hall, Inc.

Tiller, A.K. (1983).
Electrochemical aspects of microbial corrosion: an overview. *Microbial Corrosion*, **1983**, pp. 54-65. Teddington.

Tiller, A.K. and Corr, M.I. (1985).
A review of European research effort on microbial corrosion between 1950 and 1984. In *Biologically Induced Corrosion*, pp. 8-29. Ed. S.C. Dexter. Houston, Texas: NACE.

Tomei, F.A. and Mitchell, R. (1985).
Development of an alternative method for studying the role of H2-consuming bacteria in the anaerobic oxidation of iron. In *Biologically Induced Corrosion*, pp. 309-320. Ed. S.C. Dexter. Houston, Texas: NACE.

Upsher, F.J., Hodgeman, D.K.C. and Fletcher, L.E. (1993).
Hydrogen sulfide generation in shipboard oily water wastes. Part 2: Microbiological aspects (MRL Technical Report MRL-TR-93-18). Maribyrnong, Vic.: Materials Research Laboratory.

Videla, H.A. (1985).
The action of *Cladosporium resinae* growth on the electrochemical behaviour of aluminium. In *Biologically Induced Corrosion*, pp. 215-222. Ed. R.C. Dexter. Houston, Texas: NACE.

Videla, H.A. (1988).
Electrochemical interpretation of the role of microorganisms in corrosion. In *Biodeterioration*, **7**, pp. 359-371. Eds. D.R. Houghton, R.N. Smith and H.O.W. Eggins. London: Elsevier.

Videla, H.A. (1991).
Microbially induced corrosion: an updated overview. In *Biodeterioration and Biodegradation*, **8**, pp. 63-88. Ed. H.W. Rossmoore. London: Elsevier.

Videla, H.A. and Characklis, W.G. (1992).
Biofouling and microbially induced corrosion. *International Biodeterioration and Biodegradation*, **29**, pp. 195-212.

Von Wolzogen Kuhr, C.A.H. and Van der Vlugt, L.S. (1934)
Water, (den Haag), **18**, pp. 147-165. Translation in *Corrosion*, **17**, pp. 293-299, 1971.

Walch, M. and Mitchell, R. (1984).
Biological aspects of corrosion of offshore structures. *Naval Research Reviews*, **36**, pp. 13-19.

Weimer, P.J., Van Kavelaar, M.J., Michel, C.B. and Ng, T.K. (1988).
Effect of phosphate on the corrosion of carbon steel and on the composition of corrosion products in two stage continuous cultures of *Desulfovibrio desulfuricans*. *Applied and Environmental Microbiology*, **54**, pp. 386-396.

Westlake, D.W.S., Semple, K.M. and Obuekwe, C.D. (1985).
Corrosion by iron reducing bacteria isolated from oil production systems. In *Biologically Induced Corrosion*, pp. 193-198. Ed. S.C. Dexter. Houston, Texas: NACE.

Widdel, F. (1988)
Microbiology and ecology of sulfate- and sulfur-reducing bacteria. In *Biology of Anaerobic Microorganisms*, pp. 469-585. Ed. A.J.B. Zehnder. New York: Wiley.

Appendix A – Media

A.1 Maximum Recovery Diluting Fluid

Peptone (Oxoid)	1.0 g/l
Sodium chloride	8.5
Water, filtered tap	1 litre

A.2 MRL-SRB Medium

Agar (Oxoid No. 4)	5.0 g/l
Sodium chloride NaCl	5.0
Sodium lactate (70% soln)	4.0
Magnesium sulfate $MgSO_4.7H_2O$	1.0
Sodium sulfate Na_2SO_4	1.0
di-Potassium phosphate K_2HPO_4	0.5
Potassium carbonate K_2CO_2	0.5
Ammonium ferrous sulfate $(NH_4)_2SO_4.FeSO_4.6H_2O$	0.2
Tryptone (Oxoid)	0.4
Yeast Extract, desiccated (Oxoid)	0.2
Ascorbic acid	0.2
Calcium chloride $CaCl_2.2H_2O$	0.1
Water, filtered tap	1 litre

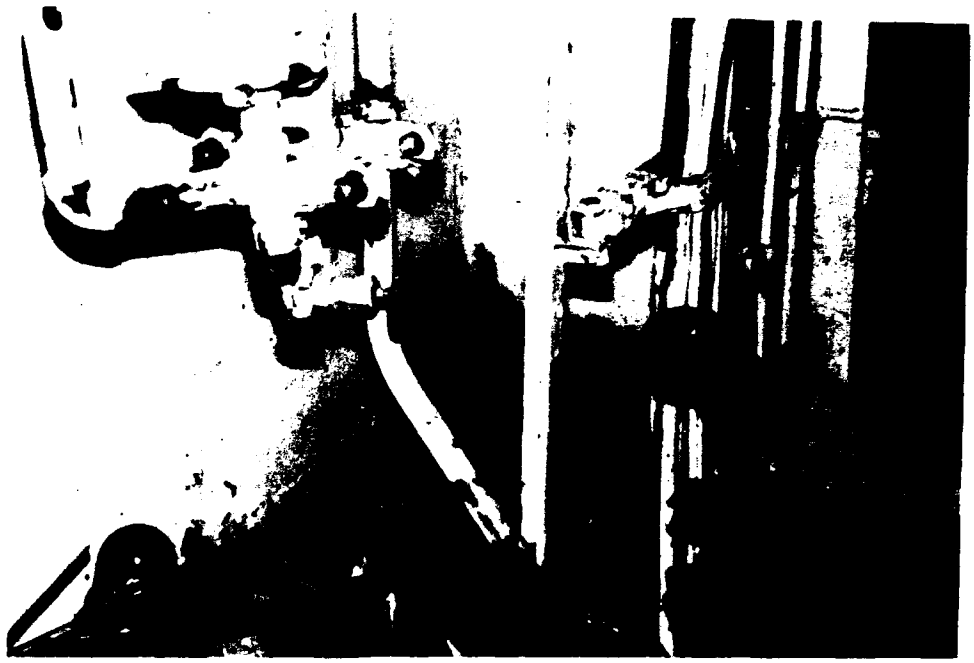


Plate 1: *Sample site H1 in Engine Room 2, HMAS Hobart.*

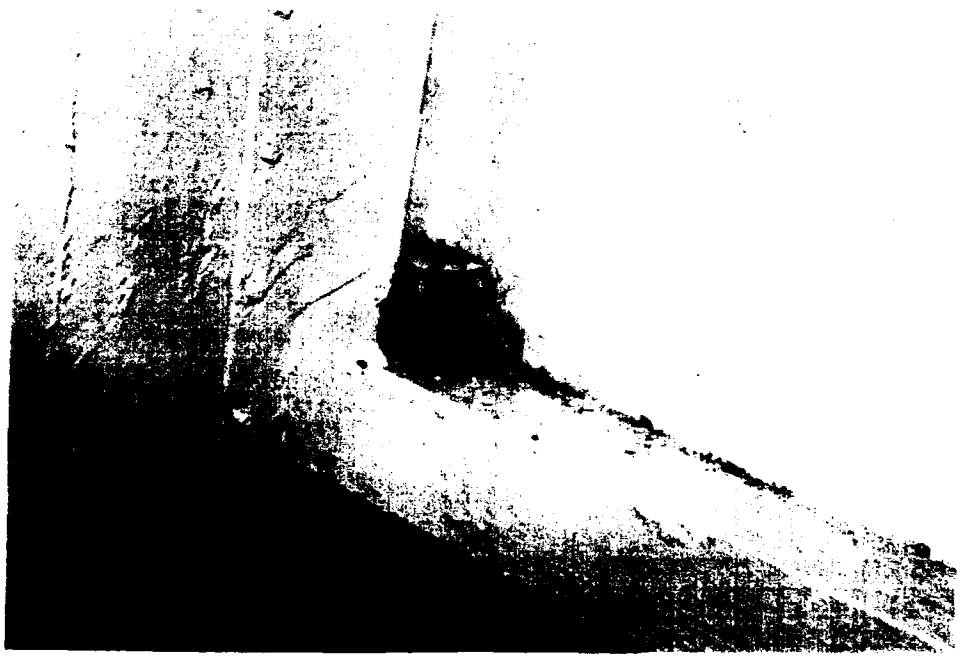


Plate 2: *Sample site H2 in Engine Room 2, HMAS Hobart.*

Plate 3: *Water pump in Engine Room 1, HMAS Hobart; sampling site H7 and H8.*

SECURITY CLASSIFICATION OF THIS PAGE **UNCLASSIFIED**

REPORT NO.	AR NO.	REPORT SECURITY CLASSIFICATION
MRL-GD-0048	AR-008-241	Unclassified

TITLE

A review of microbially induced corrosion (MIC) of steel and a preliminary investigation to determine its occurrence in naval vessels

AUTHOR(S)
John F. Upsher

CORPORATE AUTHOR
DSTO Materials Research Laboratory
PO Box 50
Ascot Vale Victoria 3032

REPORT DATE	TASK NO.	SPONSOR
May, 1993	NAV 88/126	RAN

FILE NO.	REFERENCES	PAGES
G6/4/8-4350	66	24

CLASSIFICATION/LIMITATION REVIEW DATE

CLASSIFICATION/RELEASE AUTHORITY
Chief, Ship Structures and Materials Division

SECONDARY DISTRIBUTION

Approved for public release

ANNOUNCEMENT

Announcement of this report is unlimited

KEYWORDS

Sulfate reducing bacteria	Steel corrosion	Microbially induced corrosion
SRB	MIC	

ABSTRACT

A study was made of the mechanisms of microbially induced corrosion of steels and of influencing factors. The main causative organisms were the sulfate reducing bacteria (SRB) which require little more than a wet situation with depleted oxygen, some small organic molecules and sulfate. The corrosive effect is primarily by cathodic depolarization but local abundance of sulfide and pH change are also involved. SRB were detected at one third of the corrosion sites examined on three Naval ships. They were also present in their oily water wastes which would be a source of infection of any exposed steel surfaces. Based on current information, no special measures to counter microbially induced corrosion of ship steel are recommended but antibacterial treatments warrant further investigation as remedial measures for active microbially induced corrosion (MIC) areas.

A Review of Microbially Induced Corrosion (MIS) of Steel and a Preliminary Investigation to Determine its Occurrence in Naval Vessels

John F. Upsher

(MRL-GD-0048)

DISTRIBUTION LIST

Director, MRL
Chief, Ship Structures and Materials Division
Dr D.B. Paul
Mr John F. Upsher
MRL Information Service

Chief, Defence Scientist (for CDS, FASSP, ASSCM) (1 copy only)
Director, Surveillance Research Laboratory
Director, (for Library), Aeronautical Research Laboratory
Director, Electronics Research Laboratory
Head, Information Centre, Defence Intelligence Organisation
OIC, Technical Reports Centre, Defence Central Library
Officer in Charge, Document Exchange Centre (8 copies)
Army Scientific Adviser, Russell Offices
Air Force Scientific Adviser, Russell Offices
Navy Scientific Adviser, Russell Offices
Scientific Adviser, Defence Central
Director General Force Development (Land)
Senior Librarian, Main Library, DSTOS
Librarian, MRL-Sydney - data sheet only
Librarian, H Block
UK/USA/CAN/ABCA Armies Standardisation Rep, c/- DATD (NSO) (3 copies)
Librarian, Australian Defence Force Academy
Counsellor, Defence Science, Embassy of Australia - data sheet only
Counsellor, Defence Science, Australian High Commission - data sheet only
Scientific Adviser to DSTC Malaysia, c/- Defence Adviser - data sheet only
Scientific Adviser to MRDC Thailand, c/- Defence Attache - data sheet only
Head of Staff, British Defence Research and Supply Staff (Australia)
NASA Senior Scientific Representative in Australia
INSPEC: Acquisitions Section Institution of Electrical Engineers
Head Librarian, Australian Nuclear Science and Technology Organisation
Senior Librarian, Hargrave Library, Monash University
Library - Exchange Desk, National Institute of Standards and Technology, US
Exchange Section, British Library Document Supply Centre
Periodicals Recording Section, Science Reference and Information Service, UK
Library, Chemical Abstracts Reference Service
Engineering Societies Library, US
Documents Librarian, The Center for Research Libraries, US

DNER-SS
DNM-NES